Body-ordered approximations of atomic properties

Jack Thomas

Joint work with Christoph Ortner (University of British Columbia)
and Huajie Chen (Beijing Normal University)

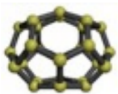
Journée de rentrée de l'équipe AN-EDP ,
Octobre 2023

Motivation

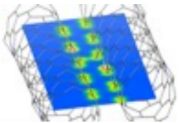
Abstract: *"We survey some recent results on the sparsity of the potential energy landscape (PEL) aimed to justify and extend the theory of machine-learning for interatomic potentials"*

Accuracy

Quantum Chemistry

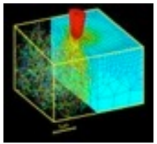


Quantum Monte Carlo

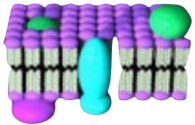


Density Functional Theory

Empirical QM



Interatomic potentials



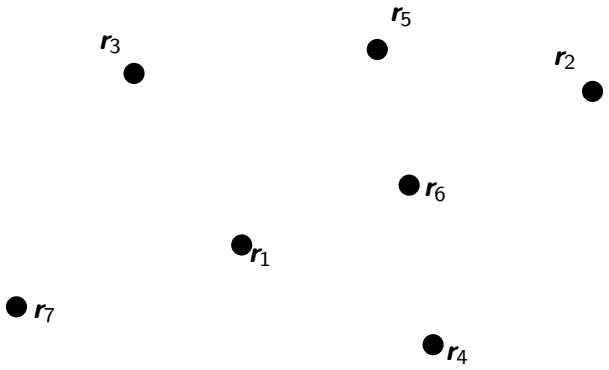
Coarse grained molecular

System size / timescale

Outline

Notation

$\boldsymbol{r} = \{\boldsymbol{r}_\ell\} \subset \mathbb{R}^d$



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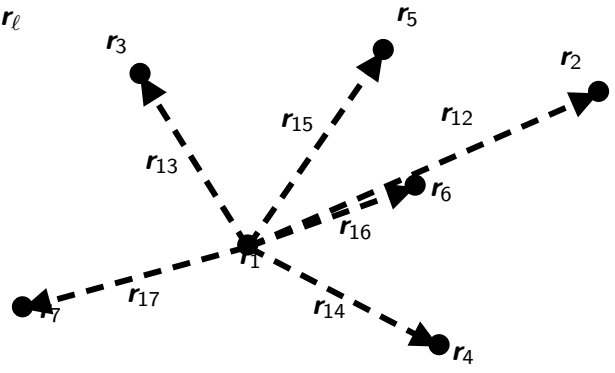
$\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$
$r_{\ell k} \coloneqq |\boldsymbol{r}_{\ell k}|$



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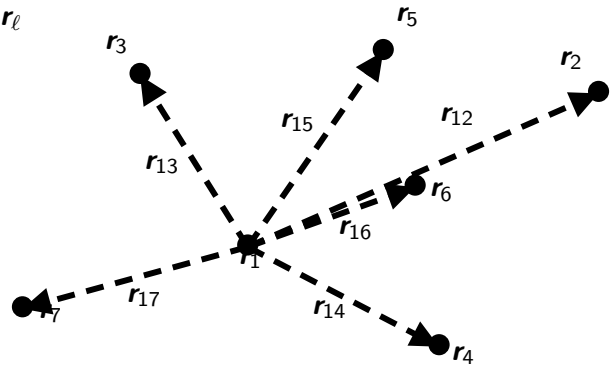

Interatomic potentials:

$$E(\boldsymbol{r}) = \sum_\ell E_\ell\big(\{\boldsymbol{r}_{\ell k}\}_{k\neq\ell}\big)$$

Classical Interatomic Potentials:

$\boldsymbol{r} = \{\boldsymbol{r}_j\} \subset \mathbb{R}^d$ – nuclei

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Embedded Atom Method (EAM):

$$E_\ell(\boldsymbol{r}) = F\Big(\sum_{k\neq\ell} \rho(r_{\ell k})\Big) + \tfrac{1}{2}\sum_{k\neq\ell} \phi(r_{\ell k})$$

Daw, Baskes. Phys. Rev. Lett. 50 (1983)
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TABLE I. Quantities used for determination of the functions and their fitted values: lattice parameter a_0; elastic constants C_{11}, C_{12}, and C_{44}; sublimation energy E_s; vacancy formation energy $E_{1v}{}^F$; the energy difference between bcc and fcc phases for Ni; and the hydrogen heat of solution and migration energy in Ni.

	Experiment	Fit
a_0(Å)	3.52[a]	3.52
C_{11} (10^{12} dynes/cm^2)	2.465[b]	2.452
C_{12} (10^{12} dynes/cm^2)	1.473[b]	1.452
C_{44} (10^{12} dynes/cm^2)	1.247[b]	1.233
E_s (eV)	4.45[c]	4.45
$E_{1v}{}^F$ (eV)	1.4[d]	1.43
$(E_{\mathrm{bcc}}-E_{\mathrm{fcc}})$ (eV)	0.06[e]	0.14
H heat of solution (eV)	0.16[f]	0.22
H migration energy (eV)	0.41[g]	0.41

[a] Ref. 13. [e] Ref. 17.
[b] Ref. 14. [f] Ref. 18.
[c] Ref. 15. [g] Ref. 19.
[d] Ref. 16.

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Overall, the most satisfactory parameter set thus far discovered is the following:

$$A = 7.049\,556\,277\,,\quad B = 0.602\,224\,558\,4\,,$$
$$p = 4\,,\quad q = 0\,,\quad a = 1.80\,, \qquad (2.7)$$
$$\lambda = 21.0\,,\quad \gamma = 1.20\,.$$

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$$E_\ell(\boldsymbol{r}) = E_\ell(\boldsymbol{r};\boldsymbol{\theta})$$

universal approximator

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neural network

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kernel method

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symmetric polynomials

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Atomic cluster expansion (ACE)

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Shapeev. Multiscale Model. Simul., 14 (2016)
Drautz. Phys. Rev. B 100 (2019)
Dusson *et al.* J. Comp. Phys. 454 (2022)

Machine Learned IPs (MLIPs)

Journal of Computational Physics 454 (2022) 110946

Atomic cluster expansion: Completeness, efficiency and stability ☆

Geneviève Dusson [a,*], Markus Bachmayr [b], Gábor Csányi [c], Ralf Drautz [d], Simon Etter [e], Cas van der Oord [c], Christoph Ortner [f]

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"All interatomic potential models make various (often ad hoc) assumptions on the PES regarding low-rank structures and locality of interactions. In general, one aims to represent a complex fully many-body PES E (exactly or approximately) as a combination of "simple" components, e.g., low-dimensional or low-rank. Here, we shall assume that E can be written in the form of a body-order expansion,

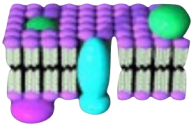
$$E\big(\{\boldsymbol{r}_1,\dots,\boldsymbol{r}_J\}\big) = \sum_{\ell=1}^{J} E_\ell\big(\{\boldsymbol{r}_{\ell k}\}_{k\neq\ell}\big)$$

$$E_\ell\big(\{\boldsymbol{r}_{\ell k}\}_{k\neq\ell}\big) = V_0 + \sum_k V_1\big(\boldsymbol{r}_{\ell k}\big) + \sum_{k_1<k_2} V_2\big(\boldsymbol{r}_{\ell k_1},\boldsymbol{r}_{\ell k_2}\big) + \cdots + \sum_{k_1<\cdots<k_N} V_N\big(\boldsymbol{r}_{\ell k_1},\dots,\boldsymbol{r}_{\ell k_n}\big), \tag{2.1}$$

with $\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$, $V_0 \in \mathbb{R}$ and $N \in \mathbb{N}$ being the maximal order of interaction."

Outline

Goal: (Qualitative) justification for the MLIP assumptions
Proof: Polynomial approximation



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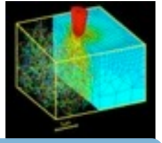
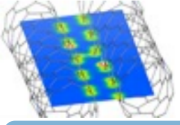
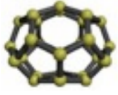


Interatomic potentials

Empirical Quantum Mechanics



Density Functional Theory



Quantum Monte Carlo

Quantum Chemistry

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_{\ell} E_{\ell}^{\mathrm{IP}}(\boldsymbol{r};\boldsymbol{\theta})$$

local decomposition into “simple” parts

Set-up

- Many-body Schrödinger equation: $\mathcal{H}_{\mathrm{tot}}\Psi = E\Psi$

KS DFT

Set-up

- Many-body Schrödinger equation: $\mathcal{H}_{\mathrm{tot}}\Psi = E\Psi$
- Born–Oppenheimer: solve for the electrons $\mathcal{H}_{\mathrm{BO}} = \mathcal{H}_{\mathrm{BO}}(\boldsymbol{r})$
  [where $\boldsymbol{r} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\mathrm{at}}}) \in (\mathbb{R}^d)^{N_{\mathrm{at}}}$]

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KS DFT

$$\mathcal{H}^{\mathrm{KS}}\psi_i(x) \coloneqq \Big(-\tfrac{1}{2}\Delta + V(x)\Big)\psi_i(x) = \varepsilon_i\psi_i(x)$$

$$\rho(x,y) \coloneqq \sum_i F(\varepsilon_i)\psi_i^\star(x)\psi_i(y), \qquad \rho(x) \coloneqq \rho(x,x)$$

where $F(\varepsilon_i)$ are the single particle occupation numbers
$V = V[\rho] \rightsquigarrow$ self-consistent field,

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- Energy: $E^{\mathrm{KS}}[\rho] = \sum_i F(\varepsilon_i)\varepsilon_i + \ldots$

Set-up

- Discretize: $\mathcal{H}\psi_i = \varepsilon_i \psi_i$, $\mathcal{H} \in \left(\mathbb{R}^{N_\mathrm{b} \times N_\mathrm{b}}\right)^{N_\mathrm{at} \times N_\mathrm{at}}$ where

Orbitals

Spectrum

$$\mathcal{H}_{\ell k, ab} := \int \phi_{\ell a}(x) \Big[-\frac{1}{2}\Delta + V(x) \Big] \phi_{kb}(x) \mathrm{d}x$$

$\{\phi_{\ell a}\}_{a=1}^{N_\mathrm{b}}$ - atom-centered localised basis functions at $\boldsymbol{r}_\ell$

[Take $S = \mathrm{id}$ by considering Löwdin transform: $S^{-T/2}\mathcal{H}S^{1/2}$]

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- **Assume**: $|\mathcal{H}_{\ell k}| \lesssim e^{-\gamma_0 r_{\ell k}}$ $\qquad [r_{\ell k} := |\boldsymbol{r}_\ell - \boldsymbol{r}_k|]$
- Band energy: $E := \sum_i F(\varepsilon_i)\varepsilon_i = \mathrm{Tr}\big(\mathcal{H}F(\mathcal{H})\big)$

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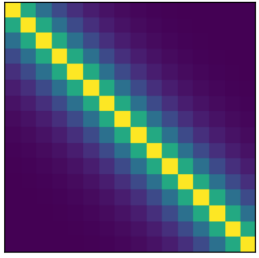
Matrix entries



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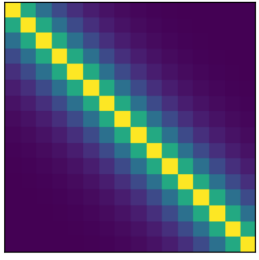
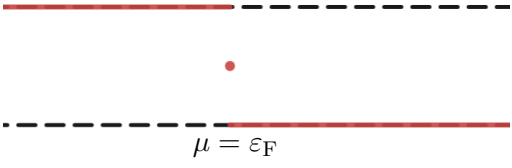
- Band energy: $E := \sum_i F(\varepsilon_i)\varepsilon_i = \mathrm{Tr}\big(\mathcal{H}F(\mathcal{H})\big)$

[Take $S = \mathrm{id}$ by considering Löwdin transform: $S^{-T/2}\mathcal{H}S^{1/2}$]

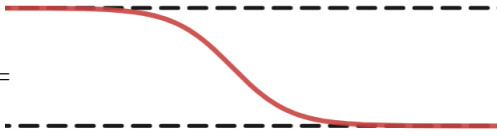
Matrix entries



$F =$



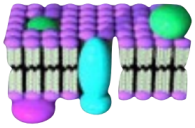
$F^\beta =$



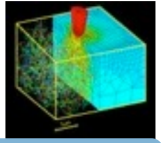
Outline

Goal: (Qualitative) justification for the MLIP assumptions
Proof: Polynomial approximation

$$E(\boldsymbol{r}) = \sum_i F(\varepsilon_i)\varepsilon_i$$

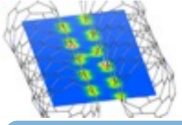


Coarse grained molecular

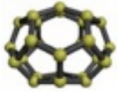


Interatomic potentials

Empirical Quantum Mechanics



Density Functional Theory



Quantum Monte Carlo

Quantum Chemistry

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_\ell E^{\mathrm{IP}}_\ell(\boldsymbol{r};\boldsymbol{\theta})$$

local decomposition into “simple” parts

Outline

Locality: Spatial Decomposition

Interatomic potentials

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_{\ell} E_{\ell}^{\mathrm{IP}}\left(\{\boldsymbol{r}_{\ell k}\}_{k \neq \ell}; \boldsymbol{\theta}\right)$$

Locality: Spatial Decomposition

- Recall:

$$E(\boldsymbol{r}) = \mathrm{Tr}\big(\mathcal{H}F(\mathcal{H})\big) = \sum_{\ell} \big[\mathcal{H}F(\mathcal{H})\big]_{\ell\ell}$$

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- Define the local observables as

$$E_{\ell}(\boldsymbol{r}) \coloneqq \big[\mathcal{H}F(\mathcal{H})\big]_{\ell\ell}$$

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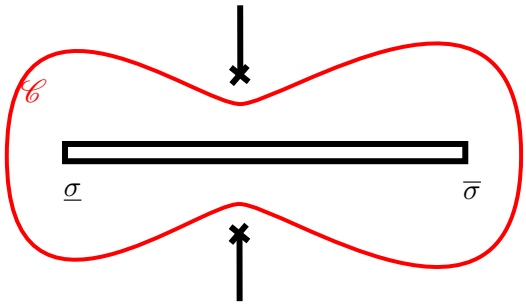
$$E_{\ell}(\boldsymbol{r}) \coloneqq \big[\mathcal{H}F(\mathcal{H})\big]_{\ell\ell} = \oint_{\mathscr{C}} zF(z)\big[(z-\mathcal{H})^{-1}\big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}$$



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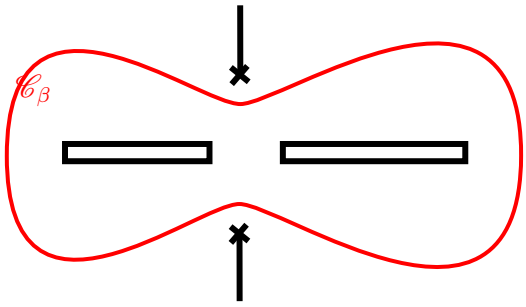

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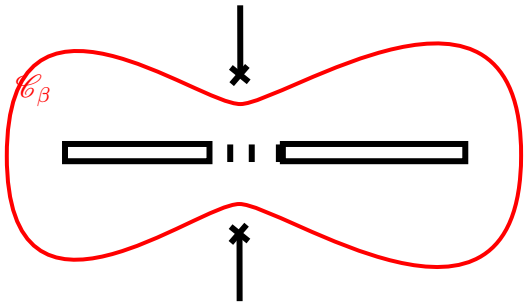

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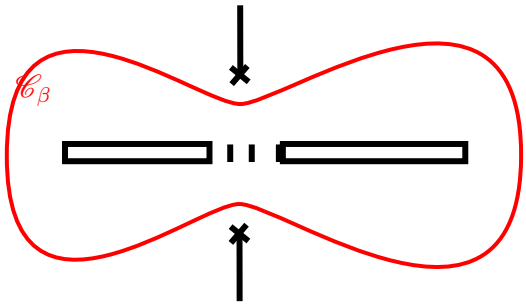
$$\begin{aligned} E_{\ell}(\boldsymbol{r}) &\coloneqq \big[\mathcal{H}F(\mathcal{H})\big]_{\ell\ell} \\ &= \oint_{\mathscr{C}} zF(z)\big[(z-\mathcal{H})^{-1}\big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i} \\ &= \int_{\mathbb{R}} xF(x)\mathrm{d}D_{\ell}(x) \end{aligned}$$



Locality: Spatial Decomposition

Tight-binding

$$E(\boldsymbol{r}) = \sum_{\ell} \left[\mathcal{H}F(\mathcal{H})\right]_{\ell\ell} = \sum_{\ell} E_{\ell}(\boldsymbol{r})$$

Interatomic potentials

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_{\ell} E_{\ell}^{\mathrm{IP}}\left(\{\boldsymbol{r}_{\ell k}\}_{r_{\ell k} < r_{\mathrm{cut}}}\right)$$

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$$\left|\frac{\partial E_\ell(\boldsymbol{r})}{\partial \boldsymbol{r}_k}\right| \leq C e^{-\eta r_{\ell k}}$$

Numerics

$\eta > 0$ depends on:

- locality of $\mathcal{H}$,
- analyticity of $z \mapsto zF(z)$,
- spectrum $\sigma(\mathcal{H})$.

Locality: Spatial Decomposition

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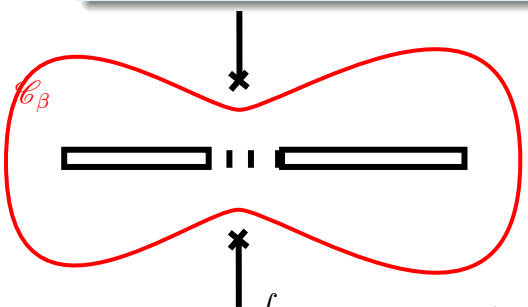

$$E_\ell = \oint_{\mathscr{C}} zF(z)\left[(z-\mathcal{H})^{-1}\right]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}$$

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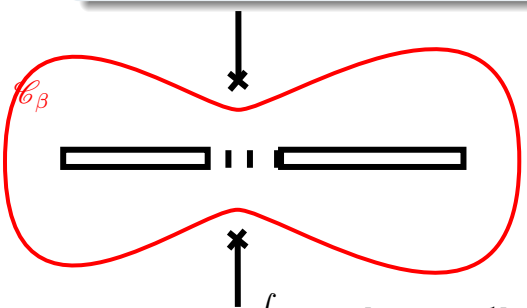

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[Chen, Ortner. Multiscale Model. Simul., 2016]
[Chen, Lu, Ortner. Arch. Rat. Mech. An., 2018]
[Ortner, JT, Chen. ESAIM: M2AN, 2020] - estimates for point defects

“Proof”: Locality Estimates

Theorem:

$$\left| \frac{\partial E_\ell(\boldsymbol{r})}{\partial \boldsymbol{r}_k} \right| \leq C e^{-\eta\, r_{\ell k}}$$

$\eta > 0$ depends on:

- locality of $\mathcal{H}$,
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"Proof": Locality Estimates

$$\frac{\partial E_\ell(\boldsymbol{r})}{\partial \boldsymbol{r}_k} = \oint_{\mathscr{C}} zF(z)\Big[(z-\mathcal{H})^{-1}\frac{\partial \mathcal{H}(\boldsymbol{r})}{\partial \boldsymbol{r}_k}(z-\mathcal{H})^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}$$

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Resolvent Estimates: Sketch for m-banded Hamiltonians

Suppose $\mathcal{H}_{\ell k} = 0$ for all $r_{\ell k} > m$.
Then, $[\mathcal{H}^N]_{\ell k} = 0$ for all $r_{\ell k} > mN$:

$$\begin{aligned}\left|(z-\mathcal{H})^{-1}_{\ell k}\right| &= \min_{P_N \in \mathcal{P}_N} \left|\left[(z-\mathcal{H})^{-1} - P_N(\mathcal{H})\right]_{\ell k}\right| \\ &\leq \min_{P_N \in \mathcal{P}_N} \left\|(z-\,\cdot\,)^{-1} - P_N\right\|_{L^\infty(\sigma(\mathcal{H}))} \\ &\lesssim e^{-\gamma N} = e^{-\frac{\gamma}{m} r_{\ell k}}\end{aligned}$$

where $\gamma \sim \operatorname{dist}\big(z, \sigma(\mathcal{H})\big)$.

Theorem:

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$\eta > 0$ depends on:

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Outline

Body-ordered approximations

Interatomic potentials

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_{\ell} E_{\ell}^{\mathrm{IP}}(\boldsymbol{r}; \boldsymbol{\theta})$$

E_ℓ - short-ranged & "simple"

More details

Body-ordered approximations

Locality: $E_\ell(\boldsymbol{r}) = E_\ell\big(\{\boldsymbol{r}_{\ell k}\}_{r_{\ell k}<r_{\rm cut}}\big) + \mathcal{O}(e^{-\eta r_{\rm cut}})$

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In practice, E_ℓ is still high-dimensional

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$$E_\ell(\boldsymbol{r}) \approx V_0 + \sum_{k\neq\ell} V_1(\boldsymbol{r}_{\ell k}) + \sum_{k_1,k_2\neq\ell} V_2(\boldsymbol{r}_{\ell k_1}, \boldsymbol{r}_{\ell k_2}) + \cdots + \sum_{k_1,\ldots,k_N\neq\ell} V_N(\boldsymbol{r}_{\ell k_1}, \ldots, \boldsymbol{r}_{\ell k_N})$$

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"In view of the fact that the Si crystal consists of atoms held in place by strong and directional bonds, it seems reasonable at first sight that the corresponding Φ could be approximated by a combination of pair and triplet potentials, V_1 and V_2."
— Stillinger, Weber. Phys. Rev. B 31 (1985)

More details

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"In this so-called many-body expansion of Φ, it is usually believed that the series has a quick convergence, therefore, the higher moments may be neglected."

— Haliciogli, Pamuk, Erkoc. Phys Status Solidi B 149 (1988)

More details

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"...the many-body potentials in general exhibit a rather slow convergence."

"It is sometimes argued that a potential expansion converges only slowly with respect to the order of the potentials and is thus impractical for use in molecular dynamics simulations."

— Drautz, Fähnle, Sanchez. J. Phys. Condens. Matter 16 (2004)

More details

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"The convergence of the expansion is slow and, for example, for bulk metals potentials V_K up to $K \geq 15$ are required."
— Drautz. Phys. Rev. B 99 (2019)

More details

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"Incorporating environment information leads to exponential convergence" $\implies$ replace V_n with V_{nN}

More details

Main idea: Polynomials are body-ordered:

$$[\mathcal{H}^n]_{\ell\ell} = \sum_{\ell_1,\dots,\ell_{n-1}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\dots\mathcal{H}_{\ell_{n-1}\ell}$$

["spatial correlations", "moments" $(\mathcal{H}^n)_{\ell\ell} = \int x^n \mathrm{d}D_\ell(x)$]

Recall

$E_\ell = \varepsilon(\mathcal{H})_{\ell\ell} = \int \varepsilon \,\mathrm{d}D_\ell$

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["spatial correlations", "moments" $(\mathcal{H}^n)_{\ell\ell} = \int x^n \mathrm{d}D_\ell(x)$*]*

Suppose $\varepsilon \approx \varepsilon_N$ where $\varepsilon_N \in \mathcal{P}_N$,
Then, $E_\ell^N \coloneqq \varepsilon_N(\mathcal{H})_{\ell\ell}$
is a body-ordered
approximation to E_ℓ

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Claim:

Proof

$$\begin{aligned} &\left|E_\ell - E_\ell^N\right| \\ &\leq \sup_{z\in\sigma(\mathcal{H})} |\varepsilon(z) - \varepsilon_N(z)| \end{aligned}$$

"convergence $\leftrightarrow$ smoothness of ε"

Main idea: Polynomials are body-ordered:

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Suppose $\varepsilon \approx \varepsilon_N$ where $\varepsilon_N \in \mathcal{P}_N$,
Then, $E_\ell^N := \varepsilon_N(\mathcal{H})_{\ell\ell}$
is a body-ordered
approximation to E_ℓ

Claim:

Proof

$$\begin{aligned} &\left|E_\ell - E_\ell^N\right| \\ &\leq \sup_{z\in\sigma(\mathcal{H})} |\varepsilon(z) - \varepsilon_N(z)| \end{aligned}$$

"convergence $\leftrightarrow$ smoothness of ε"

Linear schemes: $E_\ell^N := \varepsilon_N(\mathcal{H})_{\ell\ell}$

Recall:

$$\left|E_\ell - E_\ell^N\right| \leq \|\varepsilon - \varepsilon_N\|_{L^\infty(\sigma(\mathcal{H}))}$$

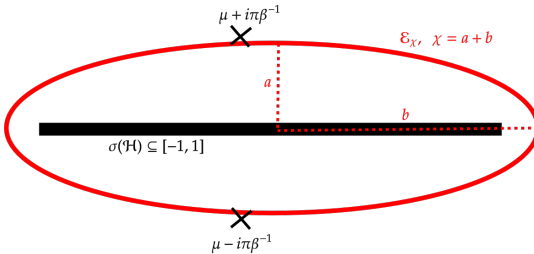
Idea #1: Upper Bounds

- Finite temperature ($\beta < \infty$): Chebyshev projection

$$\left|E_\ell - E_\ell^N\right| \leq \frac{2\|\varepsilon\|_{L^\infty(\mathcal{E}_\chi)}}{\chi - 1}\chi^{-N}$$

where F is analytic on $\mathcal{E}_\chi$.

[Proof: Chebyshev coefficients decay exponentially depending on region of analyticity]



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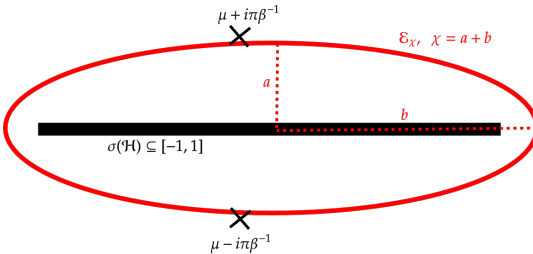

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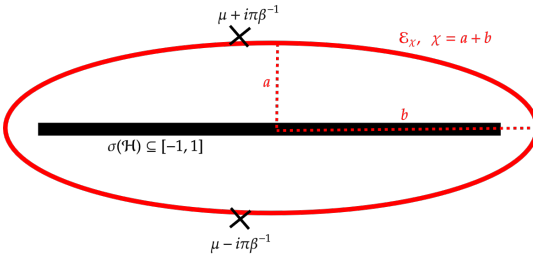

- Insulators ($g > 0$): $\exists \varepsilon_N$ s.t. [Hasson 2007]

$$\left|E_\ell - E_\ell^N\right| \leq \frac{C}{\sqrt{N}}\sqrt{\frac{2-g}{2+g}}^N$$

where g is the spectral gap.

[Symmetric gap]

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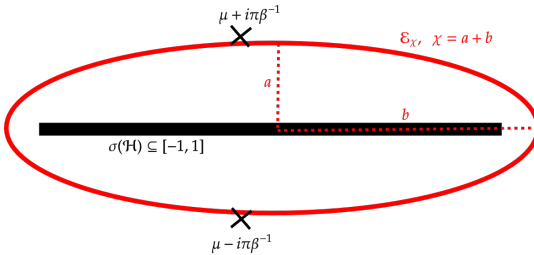

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$$\left|E_\ell - E_\ell^N\right| \le \frac{C}{\sqrt{N}}\sqrt{\frac{2-g}{2+g}}^N \sim \frac{C}{\sqrt{N}}e^{-\frac{1}{4}gN}$$

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Idea #2: Asymptotic bounds

Interpolation nodes: $X_N := \{x_j\}_{j=0}^N$

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Let $\varepsilon_N := I_{X_N}\varepsilon$ polynomial interpolation of ε on X_N

Given $A \subset \mathbb{R}$, there exists an *equilibrium measure* ω_A such that

$$\frac{1}{N}\sum_{j=0}^{N} \delta(\,\cdot\, - x_j) \rightharpoonup \omega_A \quad \Longrightarrow \quad \left\|\varepsilon - \varepsilon_N\right\|_{L^\infty(A)} \lesssim e^{-\gamma_N^\star N}$$

and $\gamma^\star = \lim_{N\to\infty} \gamma_N^\star$ is optimal.

Theorem (JT, Chen, Ortner (2022))

There exists a linear $\Theta_N : \mathbb{R}^N \to \mathbb{R}$ *such that*

$$\left| E_\ell(\boldsymbol{r}) - \Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big) \right| \leq C e^{-\gamma_N N}$$

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Idea #3: Nonlinear schemes

- Recall, local density of states D_ℓ is a (positive) measure supported on $\sigma(\mathcal{H})$ and satisfying

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$$[\mathcal{H}^n]_{\ell\ell} = \int x^n \mathrm{d}D_\ell^N(x) \qquad (n = 0, 1, \ldots, N) \qquad \longrightarrow \qquad E_\ell^N(\boldsymbol{r}) \coloneqq \int \varepsilon \, \mathrm{d}D_\ell^N,$$

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[$\mathcal{P}_N$ = polynomials degree N]

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$[\mathcal{P}_N = \text{polynomials degree } N]$

$E_\ell = \Theta_N\big(\mathcal{H}_{\ell\ell}, \ldots, [\mathcal{H}^N]_{\ell\ell}\big)$

Linear schemes:

- Chebyshev projection
  $\longrightarrow$ Kernel polynomial method[1]
- Newton–Cotes quadrature
  (equispaced nodes)
- Clenshaw–Curtis quadrature
  (Chebyshev nodes)
- General quadrature
  (with $\nu_N \rightharpoonup^\star \omega_{\sigma(\mathcal{H})}$)

Nonlinear schemes:

- Maximum entropy method[2] More
- Recursion method[3]: spectral measure corresponding to truncated tridiagonalisation of $\mathcal{H}$ More
  $\longrightarrow$ bond order potentials[4]
- Gauss quadrature More
  $\longrightarrow$ linear-scaling spectral Gauss quadrature[5]

[1] [Silver, Roeder, Voter, Kress. J. Comput. Phys. 124 (1996)]
[2] [Mead, Papanicolaou. J. Math. Phys. 25 (1984)]
[3] [Haydock, Heine, Kelly. J. Phys. C 5 (1972), 8 (1975)]
[4] [Horsfield *et al.* Phys. Rev. B 53 (1996)]
[5] [Suryanarayana *et al.* J. Mech. Phys. Solids 61 (2013)]

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where $\lim_{N\to\infty} \gamma_N = \gamma > 0$, *and* $\gamma \sim g_{\mathrm{def}} + \beta^{-1}$.

However,

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Numerics

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Theorem (JT, Chen, Ortner (2022))

Fix N *odd. There exist* $U \subset \mathbb{C}^N$ *and an analytic function* $\Theta_N \colon U \to \mathbb{C}$ *such that*

$$\left|E_\ell(\boldsymbol{r}) - \Theta_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)\right| \leq Ce^{-\eta_N N}$$

where $\lim_{N\to\infty} \eta_N = \eta > 0$, *and* $\eta \sim g + \beta^{-1}$.
Now,

- Θ_N *is a "universal" nonlinearity*
- *Eigenvalues in the gap* **do not** *affect the convergence rates*

However,

- Different Θ_N for different phases of the material
- Eigenvalues in the gap affect the convergence rate

g = gap in the essential spectrum

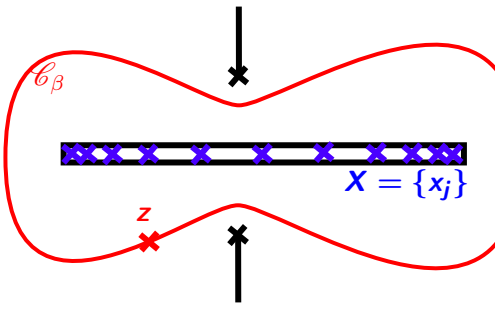
Numerics

Outline

Polynomial Approximation

Asymptotically optimal rates:

General $\sigma(\mathcal{H})$ with $\beta < \infty$ or $g > 0$



Polynomial Approximation

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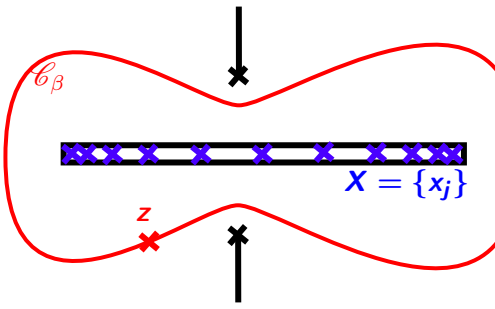

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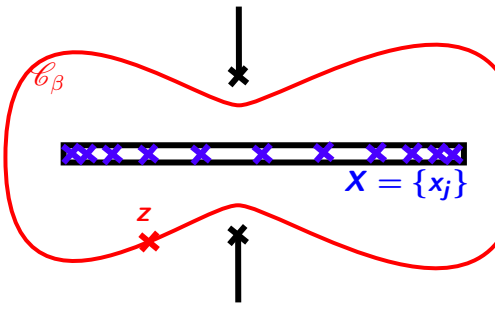

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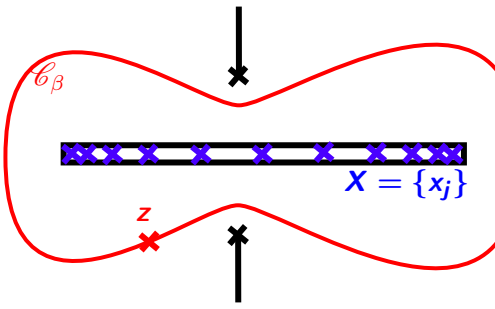

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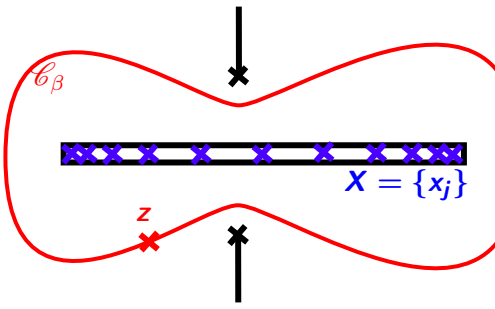
Hermite Integral formula

Let $\mathscr{C}$ contour encircling $X \cup \{x\}$,

$$I_X F(x) - F(x) = \oint_{\mathscr{C}} \frac{\ell(x)}{\ell(z)} \frac{F(z)}{x - z} \frac{\mathrm{d}z}{2\pi i}$$

where $\ell(x) := \prod_{j=0}^N (x - x_j)$ is the *node polynomial*



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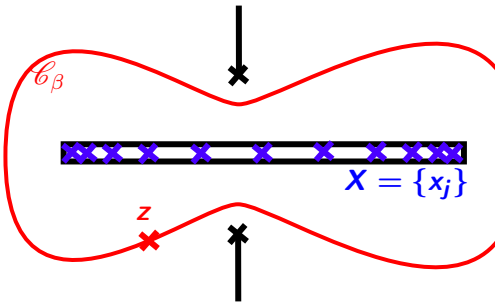


Proof:

$$\ell_j(x) = \prod_{k \neq j} \frac{x - x_k}{x_j - x_k} = \frac{\ell(x)/(x - x_j)}{\prod_{k \neq j}(x_j - x_k)} = \oint_{\mathscr{C}_j} \frac{\ell(x)/(x - z)}{\prod_{k \neq j}(z - x_k)} \frac{1}{z - x_j} \frac{\mathrm{d}z}{2\pi i} = \oint_{\mathscr{C}_j} \frac{\ell(x)}{\ell(z)} \frac{1}{x - z} \frac{\mathrm{d}z}{2\pi i}$$

Polynomial Approximation

- Hermite Integral formula $\Longrightarrow$

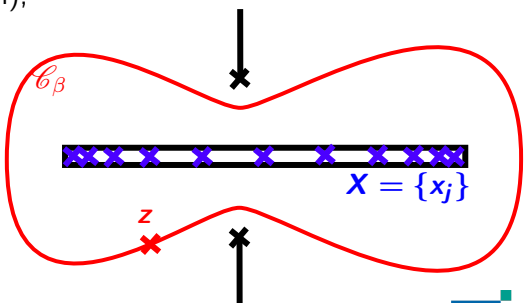
$$|I_X F(x) - F(x)| \leq \frac{\|F\|_{L^\infty(\mathscr{C})}}{2\pi \mathrm{dist}\big(\sigma(\mathcal{H}), \mathscr{C}\big)} \sup_{x\in\sigma(\mathcal{H}), z\in\mathscr{C}} \left|\frac{\ell(x)}{\ell(z)}\right|$$

where $\ell(x) := \prod_{j=0}^{N}(x - x_j)$ (node polynomial),

- **Goal:** Understand the asymptotic behaviour of

$$\left|\frac{\ell(x)}{\ell(z)}\right| \qquad \text{as } N \to \infty$$

- How to choose X?



Link to Logarithmic Potential Theory

- Define $\nu_N := \frac{1}{N}\sum_{j=0}^{N}\delta_{x_j}$ and note

$$\log\left[\left|\ell(x)\right|^{\frac{1}{N}}\right] = \frac{1}{N}\sum_{j}\log\left|x-x_j\right| = \int \log|x-t|\,\mathrm{d}\nu_N(t)$$

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- body-order approx. $\longleftrightarrow$ polynomial approx.
  $\longleftrightarrow \left|\frac{\ell(x)}{\ell(z)}\right|$ for $x \in \sigma(\mathcal{H})$ and $z \in \mathscr{C}$
  $\longleftrightarrow$ behaviour of $U^\nu(x) - U^\nu(z)$

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[Saff 2010]

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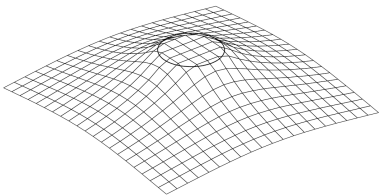

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- Q: How to compute $g_\Sigma(z) = V_\Sigma - U^{\omega_\Sigma}(z) \ge 0$?

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- Q: How to compute $g_\Sigma(z) = V_\Sigma - U^{\omega_\Sigma}(z) \geq 0$?
- (Q: How to choose X to obtain this rate of approximation?)

Link to Schwarz–Christoffel mappings

- Frostman:

$$U^{\omega_\Sigma}(z) \le V_\Sigma \qquad \text{for } z \in \mathbb{C}$$
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- $\exists!$ solution to this Green's function problem

$\Sigma = [-1, 1]$

Define $g_\Sigma(z) := \mathrm{Re}\, G_\Sigma(z)$ where

Conformal mapping problem: $G_{[-1,1]} \colon \mathbb{C}_+ \to \mathbb{C}$ s.t.

Green's function problem

Find g_Σ s.t.

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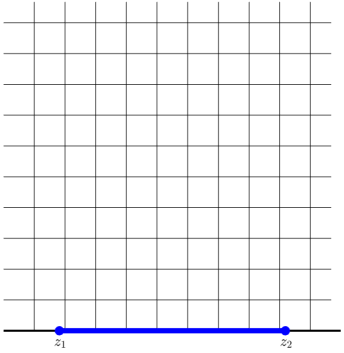
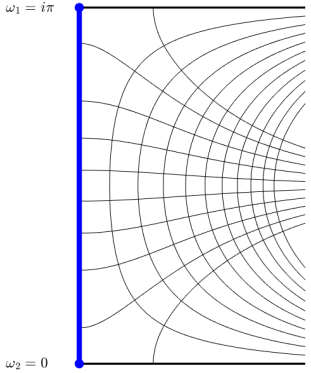


$G_{[-1,1]}$
$\longrightarrow$



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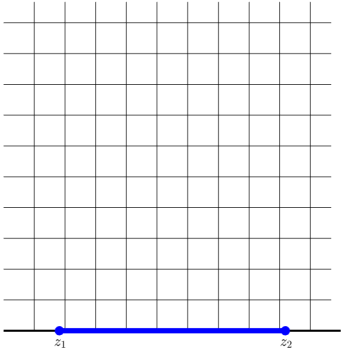

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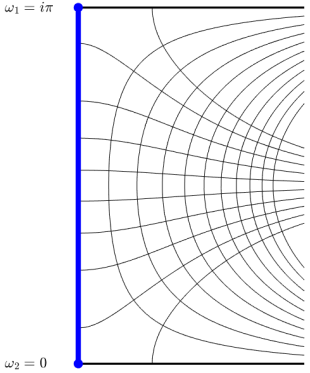

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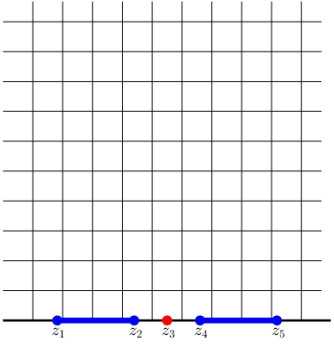

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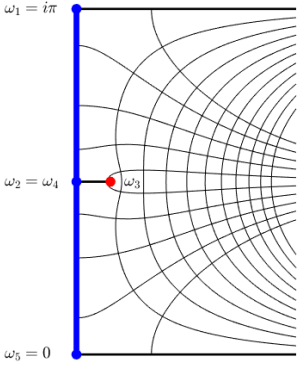

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for some $z_3 \in [a, b]$

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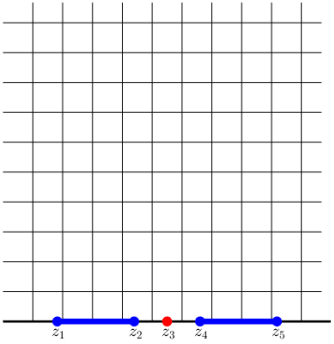

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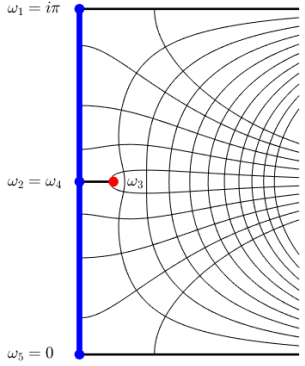

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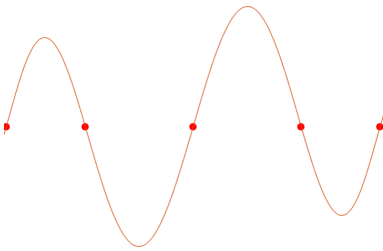

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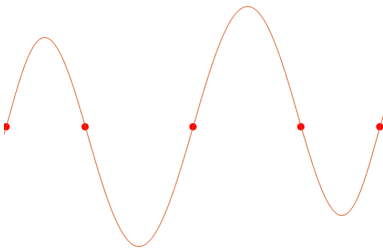

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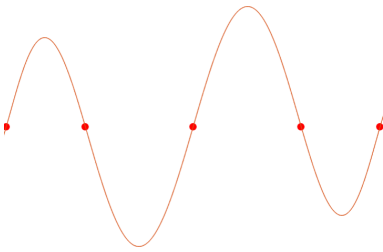

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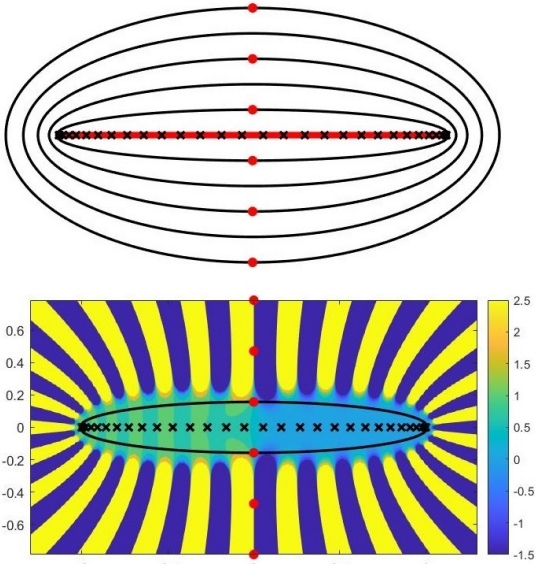

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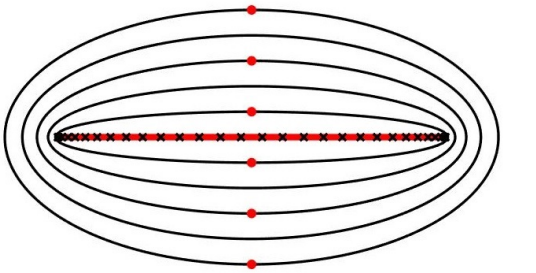

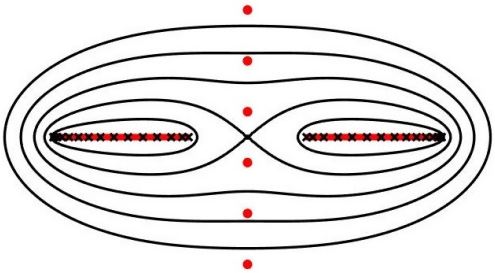

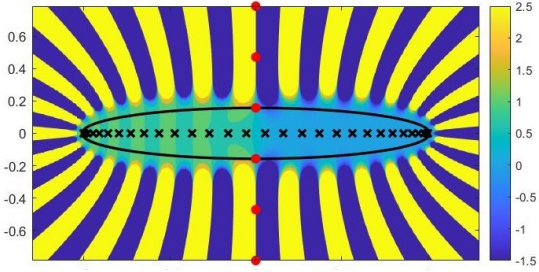

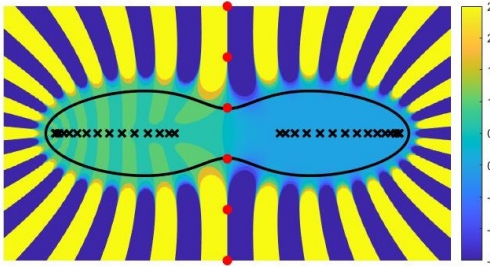

Outline

Conclusions

- $E(\boldsymbol{r}) = \sum_\ell E_\ell(\boldsymbol{r})$
  - Local pieces $\longrightarrow$ transferability
  - QM/MM schemes: size of the QM region $\sim \eta$
    [e.g. Chen, Ortner. Multiscale Model. Simul., 2016]
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- Proofs: Polynomial approximation

Arch. Rational Mech. Anal. 246 (2022) 1–60
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Body-Ordered Approximations of Atomic Properties

Jack Thomas, Huajie Chen & Christoph Ortner

Also in the paper:

- Classical vacuum cluster expansion
  [reasons for slow convergence]
- Analysis of bond-order potentials (BOP),
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  [Approximation of $\rho = F\big(\mathcal{H}[\rho]\big)$ *with* $\rho_N = F_N\big(\mathcal{H}[\rho_N]\big)$*]*
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Thank you for your attention!

What we couldn't prove (yet?):

- Forces converge in the linear schemes

$$\left|\frac{\partial E_\ell}{\partial \boldsymbol{r}_k} - \frac{\partial E_\ell^N}{\partial \boldsymbol{r}_k}\right| \lesssim e^{-\gamma r_{\ell k}} e^{-\eta N}$$

- **But**, this is a lot less obvious in the nonlinear schemes
- True if D_ℓ has *"regular n^{th} root asymptotic behaviour"*:

$$\lim_{n\to\infty} \left|p_n(z; D_\ell)\right|^{\frac{1}{n}} = e^{g_{\operatorname{supp} D_\ell}(z)}$$

  locally uniformly on $\mathbb{C} \setminus \operatorname{conv} \operatorname{supp} D_\ell$
- "Proof"

$$\left|\frac{\partial E_\ell}{\partial \boldsymbol{r}_k} - \frac{\partial E_\ell^N}{\partial \boldsymbol{r}_k}\right| \lesssim \Big[\sum_{n=0}^{\infty}\sum_{l=0}^{n} \|p_l\|^2_{L^\infty(\mathscr{C})} e^{-\eta_1 n}\Big] e^{-\eta_2 N} e^{-\gamma\, r_{\ell k}}$$

Outline

Self-consistency

- Want $\rho^\star_\ell = F\big(\mathcal{H}[\rho^\star]\big)_{\ell\ell}$,
- Approximate with $\rho_{N,\ell} = F_N\big(\mathcal{H}[\rho_N]\big)_{\ell\ell}$
  [where F_N is a body-ordered approximation of F]
- If $\rho^\star$ is *stable [linearisation is invertible]*, then there exist ρ_N such that
$$|\rho_{N,\ell} - \rho^\star_\ell| \lesssim e^{-\eta N}$$
- Can solve $\rho_{N,\ell} = F_N\big(\mathcal{H}[\rho_N]\big)_{\ell\ell}$ with the Newton iteration:
$$\rho^{i+1} = \rho^i - \big(I - DF_N(\rho^i)\big)^{-1}\big(\rho^i - F_N(\mathcal{H}[\rho^i])\big)$$

Main idea: Polynomials are body-ordered:

$$[\mathcal{H}^n]_{\ell\ell} = \sum_{\ell_1,\dots,\ell_{n-1}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\dots\mathcal{H}_{\ell_{n-1}\ell}$$

["spatial correlations", "moments" $(\mathcal{H}^n)_{\ell\ell} = \int x^n \mathrm{d}D_\ell(x)$]

Recall

$E_\ell = \varepsilon(\mathcal{H})_{\ell\ell} = \int \varepsilon \,\mathrm{d}D_\ell$

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$$\begin{aligned}\left|E_\ell - E_\ell^N\right| &= \left|\left[\varepsilon(\mathcal{H}) - \varepsilon_N(\mathcal{H})\right]_{\ell\ell}\right| \\ &\le \left\|\varepsilon(\mathcal{H}) - \varepsilon_N(\mathcal{H})\right\|_{\ell^2\to\ell^2} \\ &= \sup_{z\in\sigma(\mathcal{H})} \left|\varepsilon(z) - \varepsilon_N(z)\right|\end{aligned}$$

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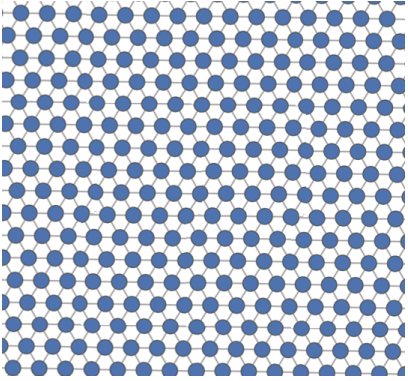
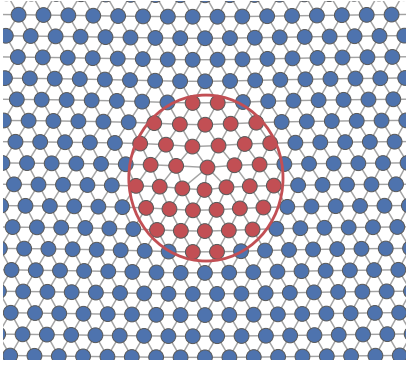
Spectrum of the Hamiltonian

$\boldsymbol{r} =$ 

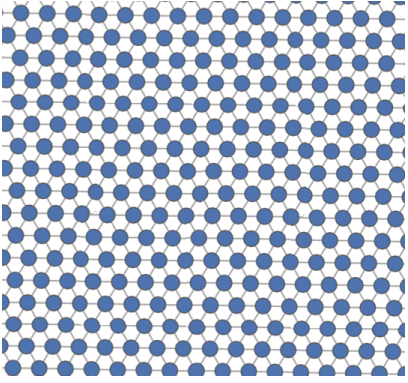
$\boldsymbol{r}^{\mathrm{def}} =$ 

Spectrum of the Hamiltonian

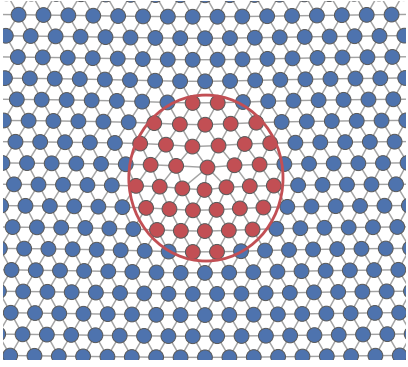
$$\{\ell\colon |\boldsymbol{r}_\ell^{\mathrm{def}}| \le R_{\mathrm{def}}\} \quad \text{finite}$$

$$\sup_{\ell\colon |\boldsymbol{r}_\ell|>R_{\mathrm{def}}} |\boldsymbol{r}_\ell^{\mathrm{def}} - \boldsymbol{r}_\ell| \le \delta$$

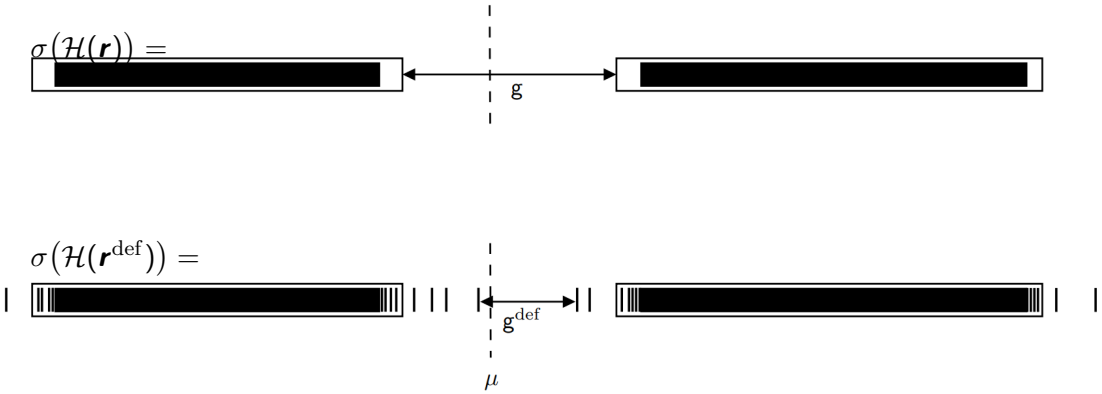
$\boldsymbol{r} =$



$\boldsymbol{r}^{\mathrm{def}} =$



Spectrum of the Hamiltonian: Insulators



Back

Spectrum of the Hamiltonian: Insulators

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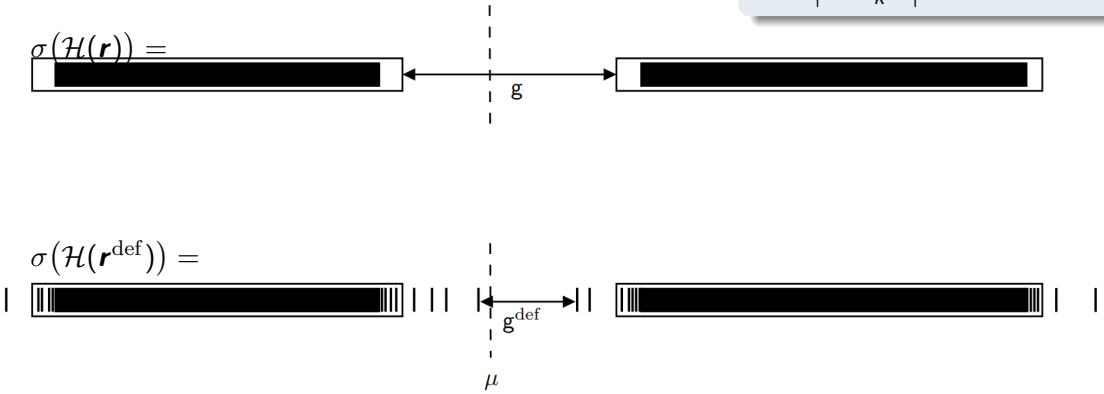

Back

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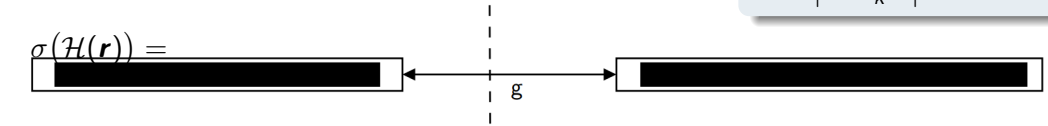
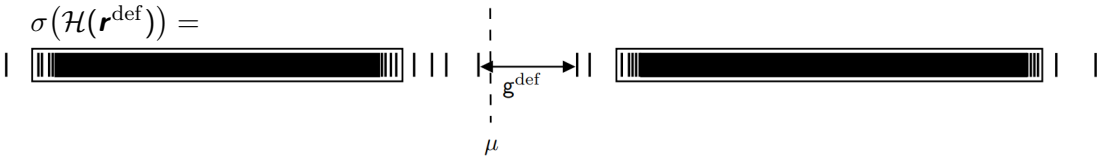


$\eta \sim \mathrm{g}$



Back

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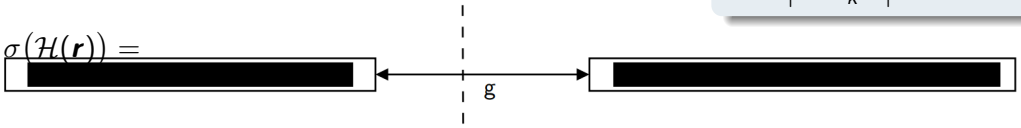
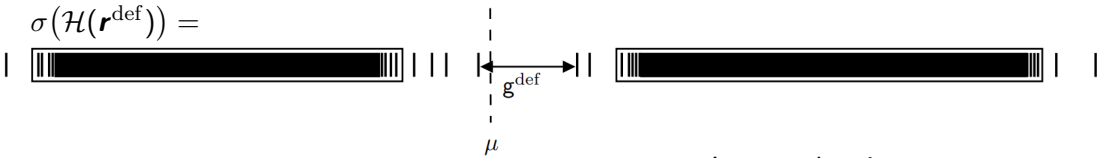


$\eta \sim \mathrm{g}$



Improved estimate:

$\eta \sim \mathrm{g} \gg \mathrm{g}^{\mathrm{def}}$

Back

(Kohn–Sham) Density Functional Theory

- Notation: $(\boldsymbol{r}_\ell, Z_\ell)$ position and species of atom ℓ,

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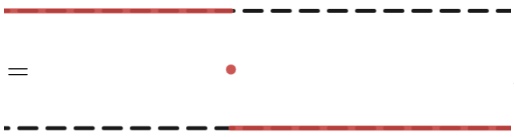
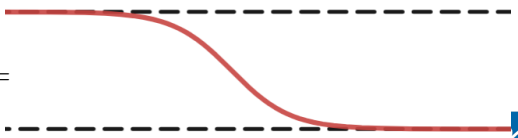
$F =$ 

$F^\beta =$ 

Back

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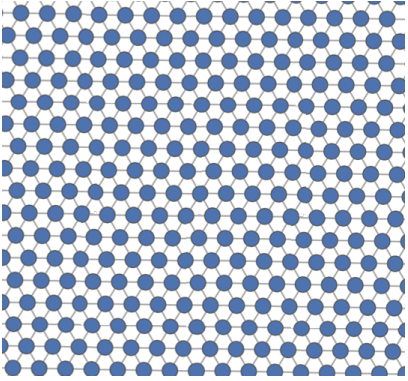
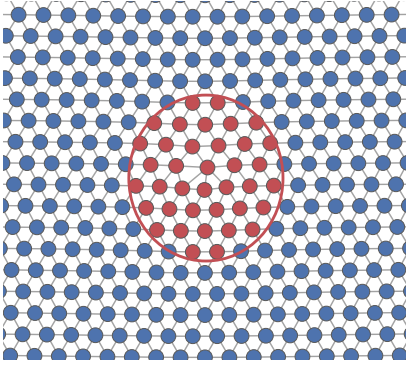
$$E^{KS}[\rho] = \sum_n \lambda_n F(\lambda_n) - \int \rho(x) V_{\mathrm{eff}}(x;\rho) + E_{\mathrm{xc}}[\rho] + \frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|}\mathrm{d}x\mathrm{d}y - \sum_m Z_m \int \frac{\rho(x)}{|x-\boldsymbol{r}_m|}\mathrm{d}x + E_{ZZ}$$

Spectrum of the Hamiltonian

$\boldsymbol{r} =$ 

$\boldsymbol{r}^{\mathrm{def}} =$ 

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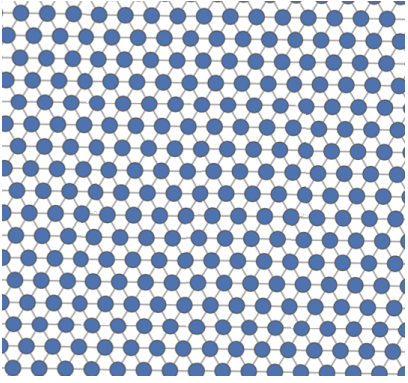

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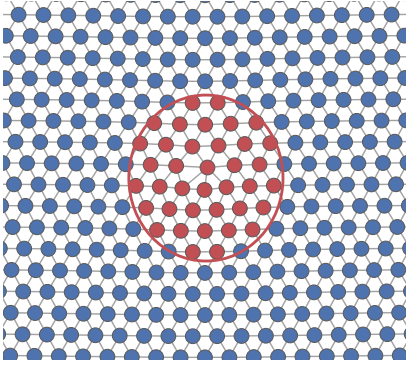
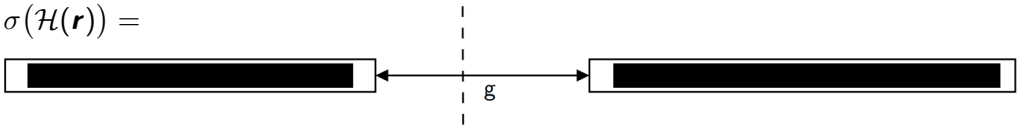
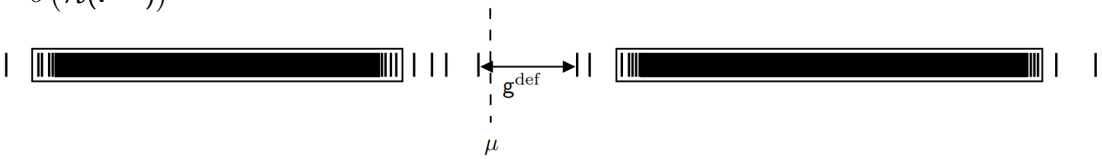


Spectrum of the Hamiltonian: Insulators

$\sigma\big(\mathcal{H}(\boldsymbol{r})\big) =$



$\sigma\big(\mathcal{H}(\boldsymbol{r}^{\mathrm{def}})\big) =$



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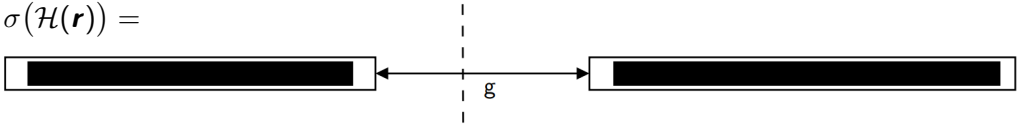
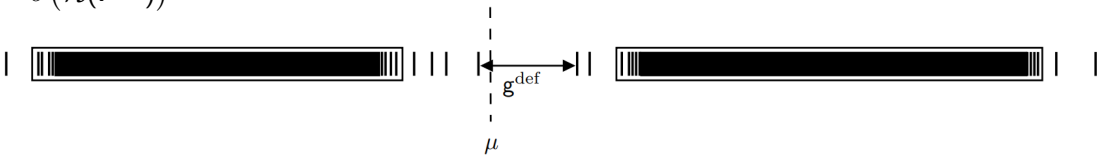


Back

$\sigma\big(\mathcal{H}(\boldsymbol{r}^{\mathrm{def}})\big) =$



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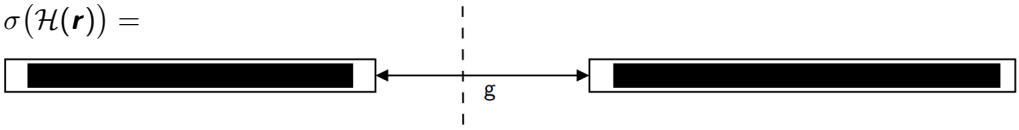

$\eta \sim \mathrm{g}$

Back

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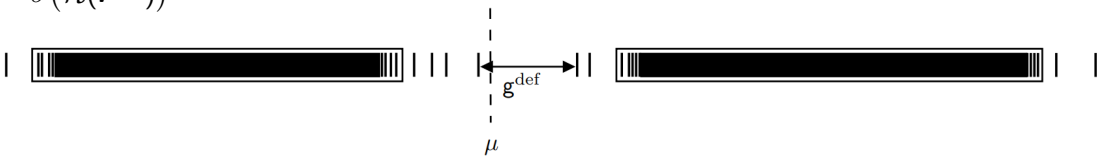

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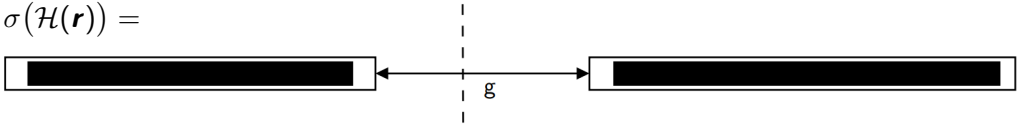

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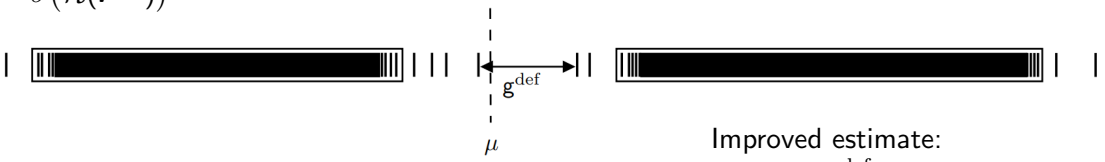
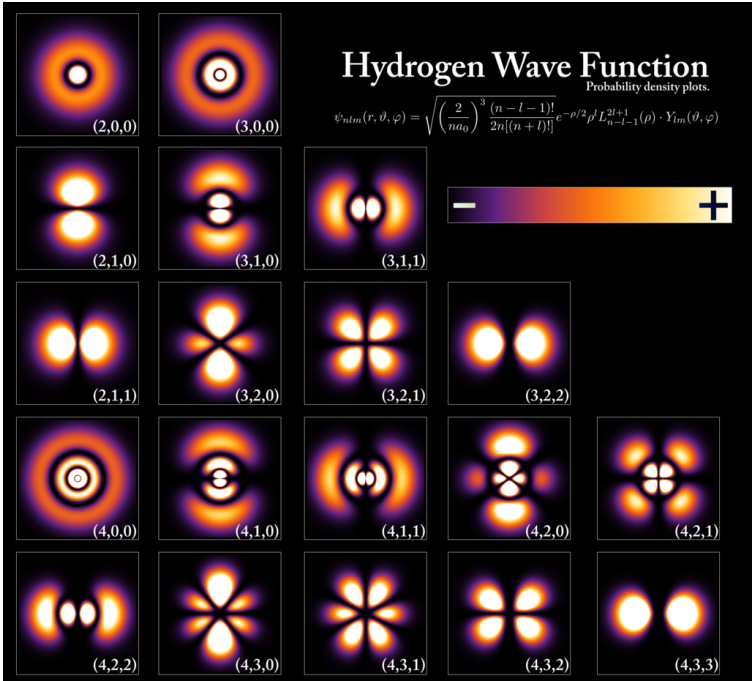


Improved estimate:

$\eta \sim \mathrm{g} \gg \mathrm{g}^{\mathrm{def}}$


Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
−
+
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
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(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

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Green's Functions for Multiply Connected Domains via Conformal Mapping*

Mark Embree†
Lloyd N. Trefethen†

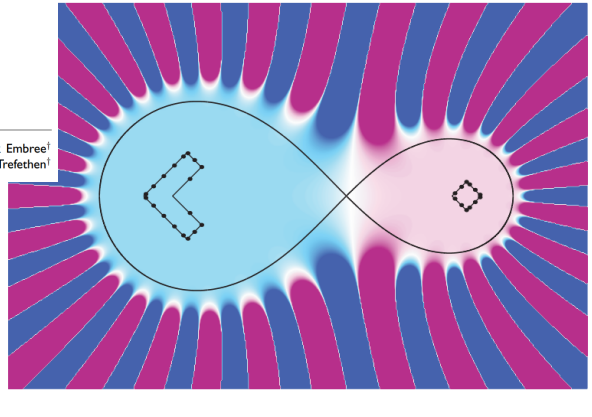

Fig. 8 *Illustration of the overconvergence phenomenon of Theorem* 2(b) *and Theorem* 4. *On the same two-polygon region as in Figure* 3, *a polynomial* $p(z)$ *is sought that approximates the values* -1 *on the hexagon and* $+1$ *on the square. For this figure,* p *is taken as the degree-*29 *near-best approximation defined by interpolation in* 30 *pre-images of roots of unity in the unit circle under the conformal map* $z = \Phi^{-1}(w)$ *(eqs.* (8) *and* (9)*); a similar plot for the exactly optimal polynomial would not look much different. The figure shows* $\mathrm{Rep}(z)$ *by a blue-red color scale together with the polygons, the interpolation points, and the figure-*8*-shaped critical level curve of the Green's function. Not just on the polygons themselves, but throughout the two lobes of the figure-*8, $\mathrm{Rep}(z)$ *comes close to the constant values* -1 *and* $+1$. *Outside, it grows very fast.*

Vacuum cluster expansion

$E\colon \bigcup_{J=0}^{\infty} \left\{ \{ \boldsymbol{r}_1, \ldots, \boldsymbol{r}_J \} \subset \mathbb{R}^3 \right\} \to \mathbb{R}$

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$$V_0 = E(\emptyset)$$

Vacuum cluster expansion

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$$V_0 = E(\emptyset)$$

$$V_1(\boldsymbol{r}_1) = E(\{\boldsymbol{r}_1\}) - E(\emptyset)$$

Vacuum cluster expansion

$E\colon \bigcup_{J=0}^{\infty} \left\{ \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_J\} \subset \mathbb{R}^3 \right\} \to \mathbb{R}$

$$
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V_0 &= E(\emptyset) \\
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V_2(\boldsymbol{r}_1, \boldsymbol{r}_2) &= E(\{\boldsymbol{r}_1, \boldsymbol{r}_2\}) - E(\{\boldsymbol{r}_1\}) - E(\{\boldsymbol{r}_2\}) + E(\emptyset)
\end{aligned}
$$

Vacuum cluster expansion

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&\vdots \\
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Then,

$$E(\{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_J\}) \approx \sum_{n=0}^{N} \sum_{j_1 < \cdots < j_n} V_n(\boldsymbol{r}_{j_1}, \ldots, \boldsymbol{r}_{j_n})$$

Exact for $N = J$.

Vacuum cluster expansion

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Convergence? Rate of convergence? Not clear!

"An intuitive explanation for this slow convergence is that we are building an interaction law for a condensed or possibly even crystalline phase material from clusters in vacuum where the bonding chemistry is significantly different."

Vacuum cluster expansion

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Exact for $N = J$.

Convergence? Rate of convergence? Not clear!

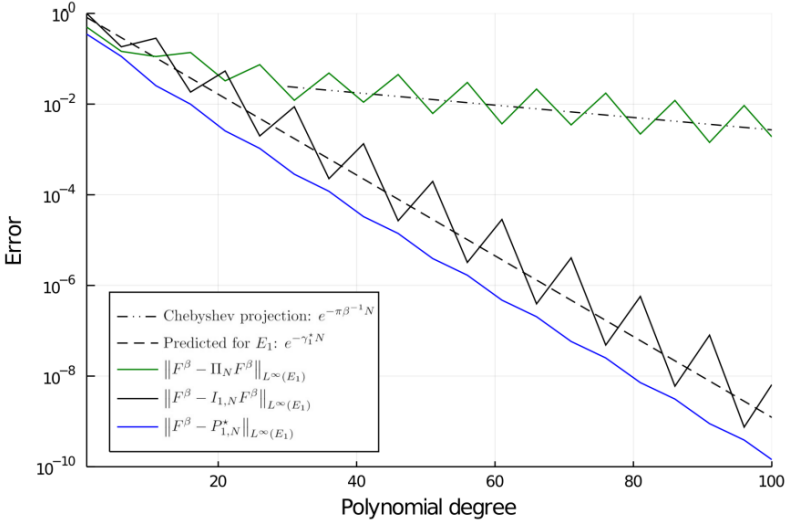
Instead:

Replace V_n with V_{nN}

"An intuitive explanation for this slow convergence is that we are building an interaction law for a condensed or possibly even crystalline phase material from clusters in vacuum where the bonding chemistry is significantly different."

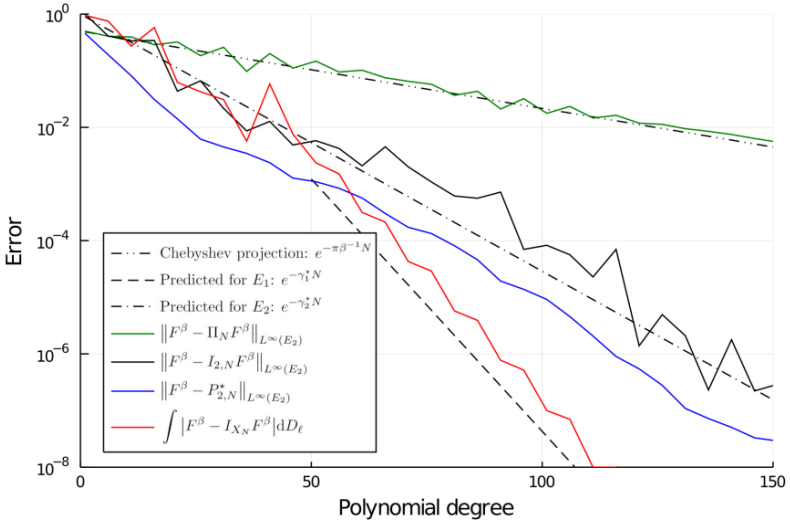
Numerical experiments: "defect-free"

- Approximation domain $E_1 = [-1, -0.2] \cup [0.2, 1]$



Numerical experiments: with defect

- Approximation domain $E_2 = E_1 \cup [-0.06, -0.03]$



Back

Maximum entropy method

- Fix $[a, b] \supset \sigma(\mathcal{H})$, maximise

$$S(P) := -\int_a^b \big[P(x)\log P(x) - P(x)\big]\,\mathrm{d}x + \sum_{n=0}^{N} \lambda_n \left(\int_a^b x^n P(x)\mathrm{d}x - [\mathcal{H}^n]_{\ell\ell} \right)$$

- Leads to

$$P_N(x) = e^{-\sum_{n=0}^{N} \lambda_n x^n} \qquad \text{s.t. first } N \text{ moments}$$

- Moreover, if $\{(\mathcal{H}^n)_{\ell\ell}\}$ is completely monotone, then $\exists! P$.

Nonlinear schemes: Recursion method

- Let $\{p_n\}$ orthogonal polynomials with respect to D_ℓ:

$$b_{n+1}p_{n+1}(x) = (x - a_n)p_n(x) - b_n p_{n-1}(x) \qquad \text{[Lanczos recursion]}$$

define

$$T_N \coloneqq \begin{pmatrix} a_0 & b_1 & & \\ b_1 & a_1 & \ddots & \\ & \ddots & \ddots & b_N \\ & & b_N & a_N \end{pmatrix} = \Big(\int p_i(x) x p_j(x) \mathrm{d}D_\ell(x) \Big)_{0 \le i,j \le N},$$

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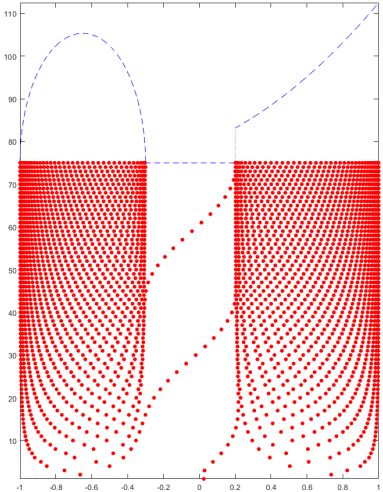

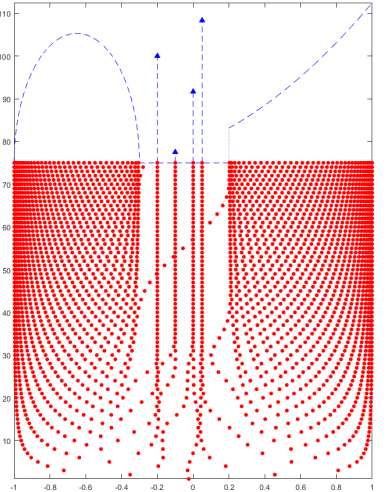

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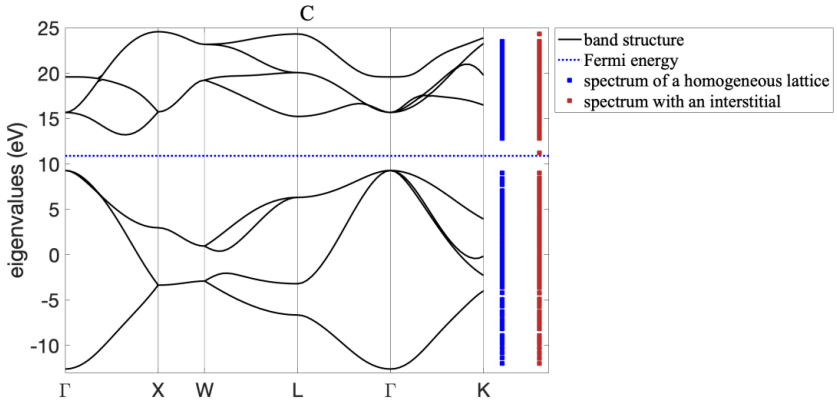
- Can show that $E_\ell^N = \Theta\left(\mathcal{H}_{\ell\ell}, \ldots, (\mathcal{H}^{2N+1})_{\ell\ell}\right)$ where $\Theta\colon \mathbb{C}^{2N+1} \to \mathbb{C}$ is analytic in open neighbourhoods of "admissible moment sequences"

Numerical Experiments



[Ortner, JT, Chen. ESAIM: M2AN, 2020]

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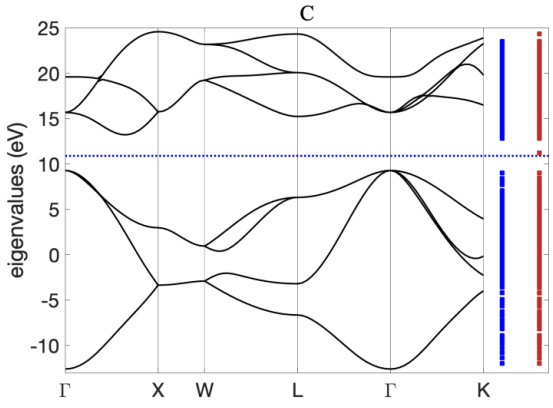

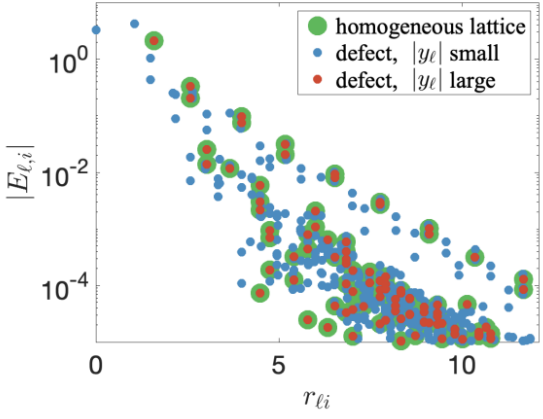

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(a) Decay of site energy derivatives.

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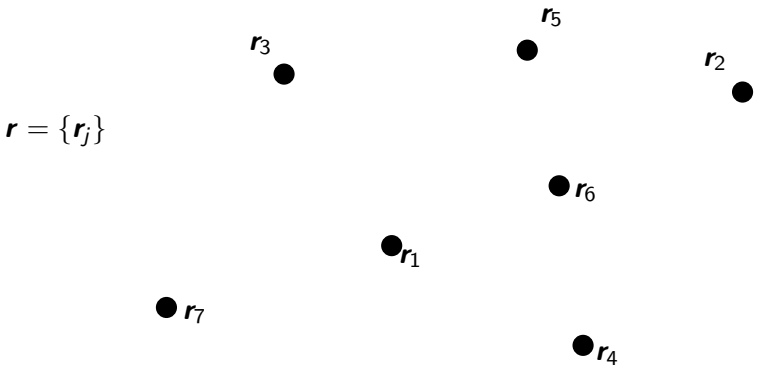

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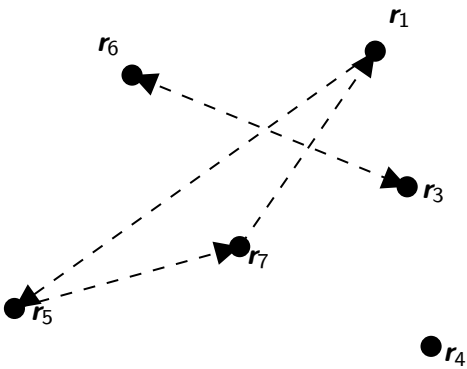

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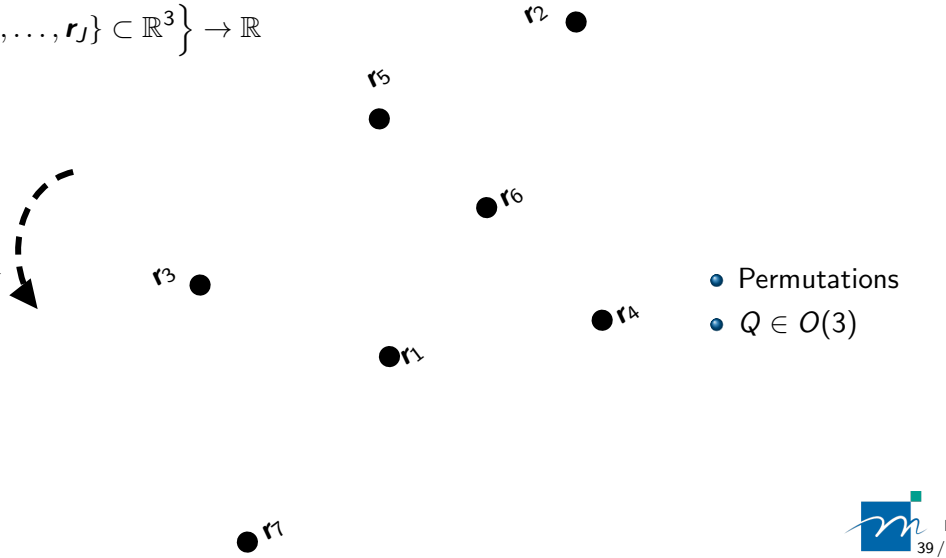
$$Q\boldsymbol{r} \coloneqq \{Q\boldsymbol{r}_j\}$$



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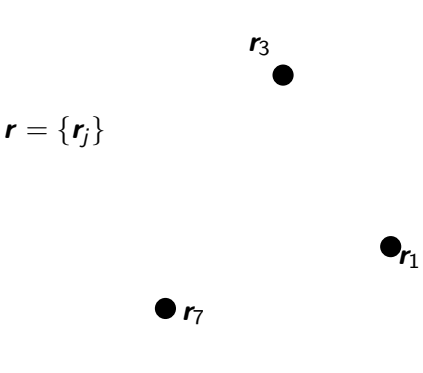
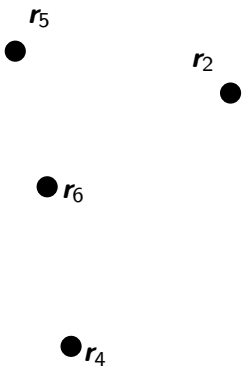
— Bachmayr *et al.* J. Comp. Phys. 454 (2022)





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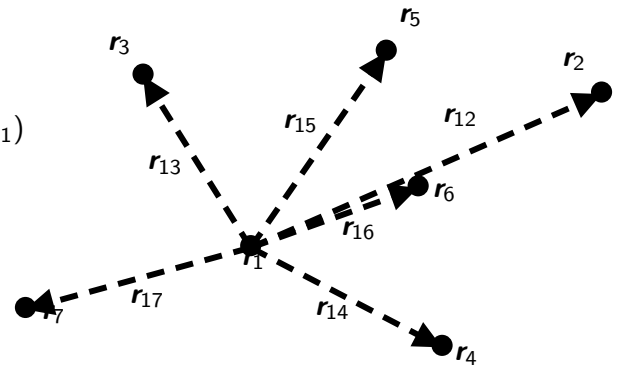

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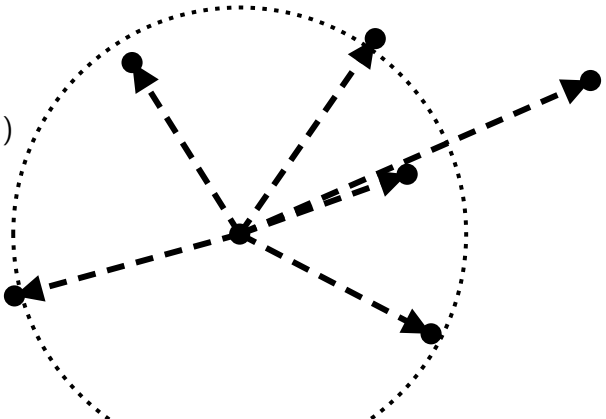

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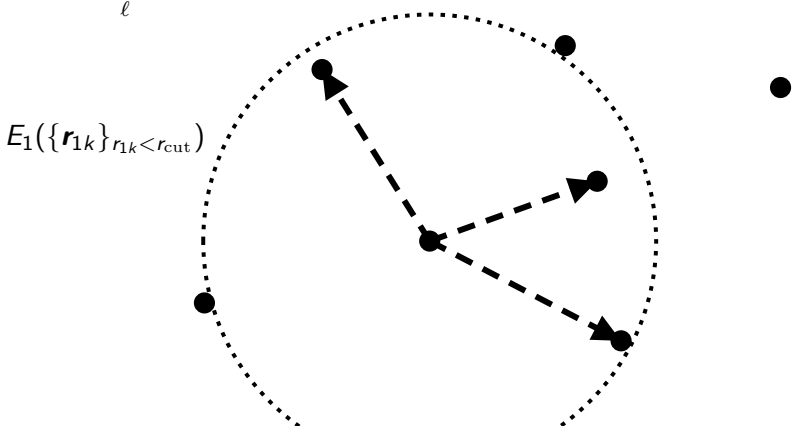

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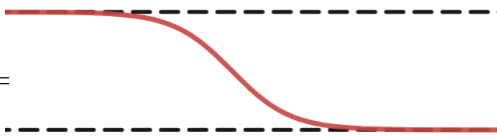

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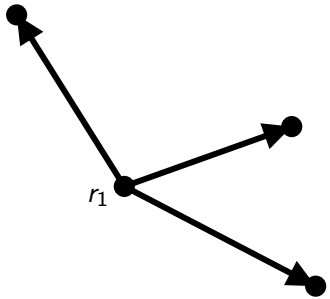

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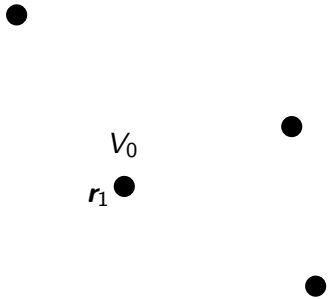

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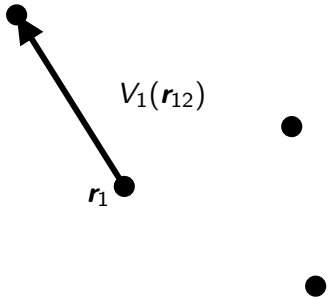
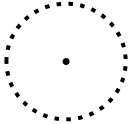


$E_1 =$ V_0 $+$

$=$



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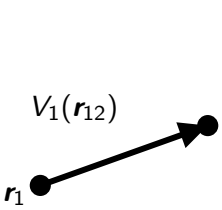

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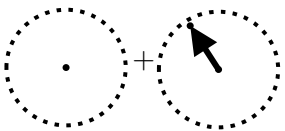

Atomic Cluster Expansion

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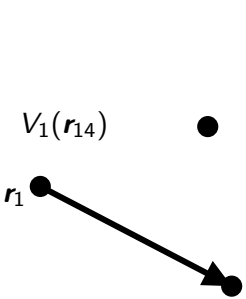

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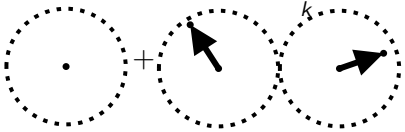

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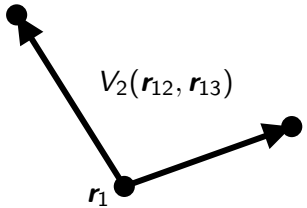

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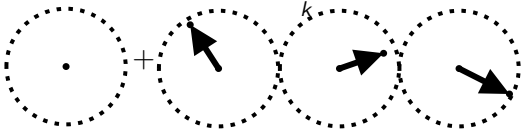

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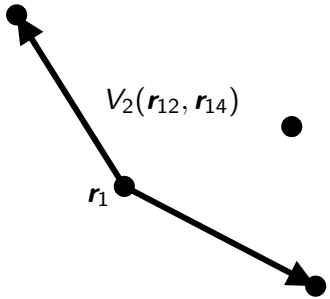

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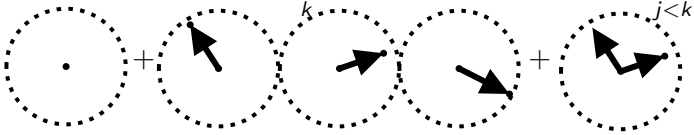
$$=$$



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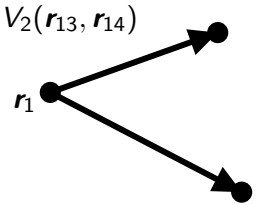

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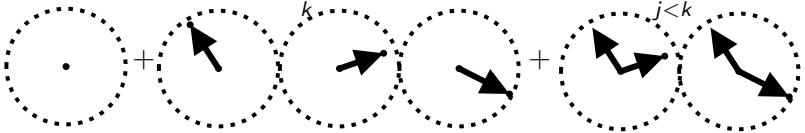

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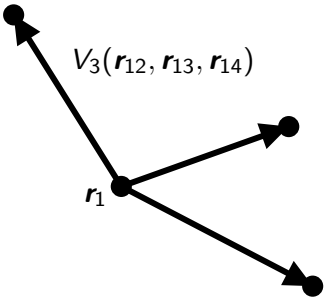

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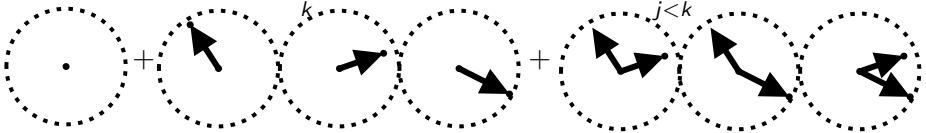
$$= \quad + \quad + \quad + \cdots$$



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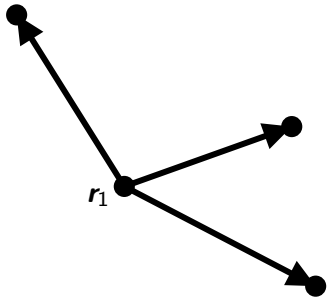

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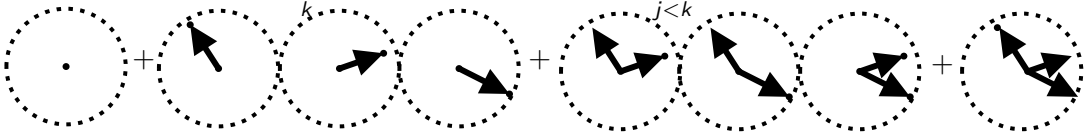

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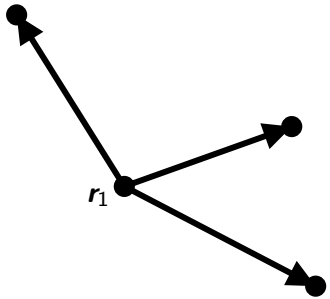

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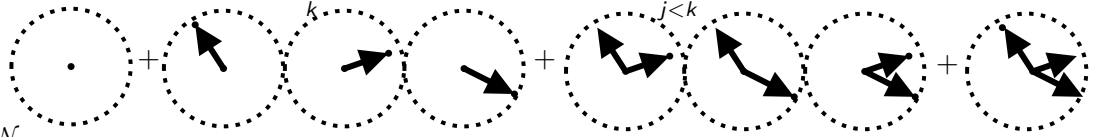

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Computationally efficient? For $J \gg \mathcal{N}$, naively scales like $\binom{J}{\mathcal{N}} \sim \frac{J^{\mathcal{N}}}{\mathcal{N}!}$

ACE: Approximate $V_N(\boldsymbol{R})$ where $\boldsymbol{R} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \in \mathbb{R}^{3N}$

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ACE: Trick

(Naive) Cost: compute basis $N!$, evaluate following $\binom{J}{N}$

$$\sum_{j_1<\cdots<j_N} \widetilde{V}_N(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \sum_{\boldsymbol{nl}i} \widetilde{c}_{\boldsymbol{nl}i} \sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N})$$

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(Naive) Cost: compute basis $N!$, evaluate following $\binom{J}{N}$

$$\sum_{j_1<\cdots<j_N} \widetilde{V}_N(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \sum_{\boldsymbol{nli}} \widetilde{c}_{\boldsymbol{nli}} \sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nli}}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N})$$

$$\sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nli}}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1\neq\cdots\neq j_N} \mathcal{B}_{\boldsymbol{nli}}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nli}}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) + W_{N-1}$$

$$\frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nli}}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nli})} \sum_{\sigma\in S_N} \phi_{\boldsymbol{nlm}}\left(\boldsymbol{r}_{j_{\sigma(1)}},\ldots,\boldsymbol{r}_{j_{\sigma(N)}}\right)$$

$$= \sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nli})} \sum_{j_1,\ldots j_N} \prod_{\alpha=1}^{N} \phi_{n_\alpha l_\alpha m_\alpha}\left(\boldsymbol{r}_{j_\alpha}\right)$$

$$= \boxed{\sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nli})} \prod_{\alpha=1}^{N} \sum_{j=1}^{J} \phi_{n_\alpha l_\alpha m_\alpha}(\boldsymbol{r}_j)}$$

ACE: Trick

(Naive) Cost: compute basis $N!$, evaluate following $\binom{J}{N}$

$$\sum_{j_1<\cdots<j_N} \widetilde{V}_N(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \sum_{\boldsymbol{nl}i} \widetilde{c}_{\boldsymbol{nl}i} \sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N})$$

$$\sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1\neq\cdots\neq j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) + W_{N-1}$$

$$\frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nl}i)} \sum_{\sigma\in S_N} \phi_{\boldsymbol{nlm}}\big(\boldsymbol{r}_{j_{\sigma(1)}},\ldots,\boldsymbol{r}_{j_{\sigma(N)}}\big)$$

$$= \sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nl}i)} \sum_{j_1,\ldots j_N} \prod_{\alpha=1}^{N} \phi_{n_\alpha l_\alpha m_\alpha}(\boldsymbol{r}_{j_\alpha})$$

$$= \boxed{\sum_{\boldsymbol{m}} \mathcal{C}_{\boldsymbol{m}}^{(\boldsymbol{nl}i)} \prod_{\alpha=1}^{N} \sum_{j=1}^{J} \phi_{n_\alpha l_\alpha m_\alpha}(\boldsymbol{r}_j)} =: B_{\boldsymbol{nl}i}(\{\boldsymbol{r}_j\})$$

ACE: Trick

(Naive) Cost: compute basis $N!$, evaluate following $\binom{J}{N}$

$$\sum_{j_1<\cdots<j_N} \widetilde{V}_N(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \sum_{\boldsymbol{nl}i} \widetilde{c}_{\boldsymbol{nl}i} \sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N})$$

$$\sum_{j_1<\cdots<j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1\neq\cdots\neq j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) + W_{N-1}$$

$$\frac{1}{N!} \sum_{j_1,\ldots j_N} \mathcal{B}_{\boldsymbol{nl}i}(\boldsymbol{r}_{j_1},\ldots,\boldsymbol{r}_{j_N}) = \frac{1}{N!} \sum_{j_1,\ldots j_N} \sum_{\boldsymbol{m}} \boldsymbol{C}^{(\boldsymbol{nl}i)}_{\boldsymbol{m}} \sum_{\sigma\in S_N} \phi_{\boldsymbol{nlm}}\big(\boldsymbol{r}_{j_{\sigma(1)}},\ldots,\boldsymbol{r}_{j_{\sigma(N)}}\big)$$

$$= \sum_{\boldsymbol{m}} \boldsymbol{C}^{(\boldsymbol{nl}i)}_{\boldsymbol{m}} \sum_{j_1,\ldots j_N} \prod_{\alpha=1}^{N} \phi_{n_\alpha l_\alpha m_\alpha}(\boldsymbol{r}_{j_\alpha})$$

$$= \boxed{\sum_{\boldsymbol{m}} \boldsymbol{C}^{(\boldsymbol{nl}i)}_{\boldsymbol{m}} \prod_{\alpha=1}^{N} \sum_{j=1}^{J} \phi_{n_\alpha l_\alpha m_\alpha}(\boldsymbol{r}_j)} =: B_{\boldsymbol{nl}i}(\{\boldsymbol{r}_j\})$$

ACE = expansion in terms of the basis $\bigcup_{N=0}^{\infty}\{B_{\boldsymbol{nl}i} : \boldsymbol{n},\boldsymbol{l}\in\mathbb{N}^N,\ldots\}$

$\Sigma = [-1, a] \cup [b, 1]$

Define $g_\Sigma(z) := \mathrm{Re} G_\Sigma(z)$ where

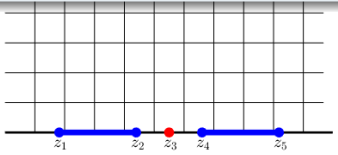
Green's function problem

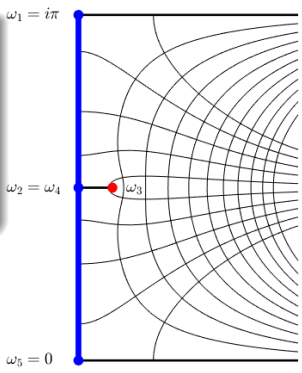
Find g_Σ s.t.

- $\Delta g_\Sigma = 0$ on $\mathbb{C} \setminus \Sigma$,
- $g_\Sigma(z) \sim \log|z|$ as $z \to \infty$,
- $g_\Sigma = 0$ on Σ.

$z_3 \in [a, b]$ s.t. $G_\Sigma(a) = G_\Sigma(b)$

$$z_3 = \frac{\displaystyle\int_a^b \frac{\zeta}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}{\displaystyle\int_a^b \frac{1}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}$$





$\Sigma = [-1, a] \cup [b, 1]$

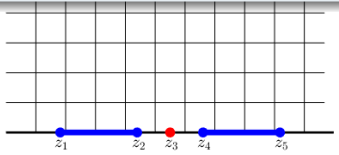
Define $g_\Sigma(z) := \mathrm{Re} G_\Sigma(z)$ where

$$G_{[-1,a]\cup[b,1]}(z) = \int_1^z \frac{\zeta - z_3}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta,$$

for some $z_3 \in [a, b]$

$z_3 \in [a, b]$ s.t. $G_\Sigma(a) = G_\Sigma(b)$

$$z_3 = \frac{\displaystyle\int_a^b \frac{\zeta}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}{\displaystyle\int_a^b \frac{1}{\sqrt{\zeta+1}\sqrt{\zeta-a}\sqrt{\zeta-b}\sqrt{\zeta-1}}\mathrm{d}\zeta}$$



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